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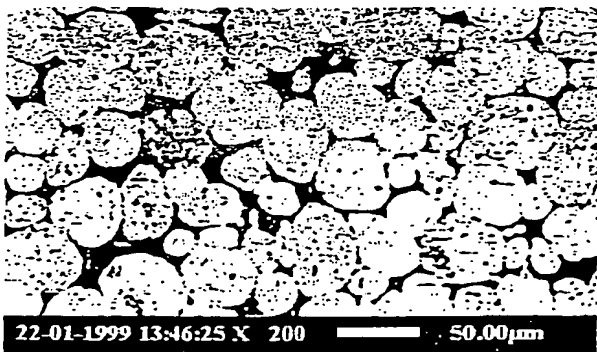
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(54) Title: LITHIUM POWDER ANODE, LITHIUM BATTERY USING THE SAME AND PREPARATION THEREOF



(57) Abstract: The present invention relates to a lithium powder anode for lithium battery comprising a metal electrode and a powdery lithium metal layer coated thereon, characterized in that said powdery lithium metal layer is prepared from powdery lithium metal. The present invention further provides a process for the preparation of the lithium powder anode and a lithium battery using said lithium powder anode. The lithium powder anode according to the present invention can suppress the formation and growth of a dendrite of lithium metal on the surface of the anode.

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LITHIUM POWDER ANODE, LITHIUM BATTERY USING THE SAME AND PREPARATION THEREOF

TECHNICAL FIELD

5 The present invention relates to an anode made of lithium (Li) powder, lithium battery using the same and the preparation method thereof. The present invention particularly relates to an anode made of lithium metal which is prepared under a oxygen-free condition, to a primary lithium battery using said anode made of lithium powder, of which the high-temperature storage stability and the voltage dropping phenomenon at instant
10 discharge are improved, to a secondary lithium battery using said anode made of lithium powder, of which a deterioration of battery capacity during the charging and discharging is suppressed, an inner circuit shortage is prohibited and the stability is greatly increased, and to the method of preparing the same.

 Due to the recent development of mobile electronic and communication devices, and
15 also from an environment and energy concern, a necessity for primary batteries (non-rechargeable) and secondary batteries (rechargeable) increases more greatly. In general, a battery consists of three main components (an anode, a cathode and an electrolyte) and other components such as a separator, an outer can, etc. Examples of batteries which have been developed and marketed till now include a manganese dry battery [$\text{MnO}_2(\text{cathode}) \parallel \text{ZnCl}_2$
20 or $\text{NH}_4\text{Cl}(\text{electrolyte}) \parallel \text{Zn}(\text{anode})$], an alkaline battery [$\text{MnO}_2 \parallel \text{KOH}$ or $\text{NaOH} \parallel \text{Zn}$], a silver oxide battery [$\text{Ag}_2\text{O} \parallel \text{KOH} \parallel \text{Zn}$] in which the weak acidic electrolyte of the manganese dry battery is replaced with a strong acidic electrolyte such as potassium hydroxide, a fluorinated graphite-lithium battery [$(\text{CF})_n \parallel \text{LiBF}_4 \parallel \gamma\text{-BL}$], a manganese dioxide-lithium battery [$\text{MnO}_2 \parallel \text{LiCF}_3\text{SO}_3/\text{PC}+\text{DME} \parallel \text{Li}$], a vanadium-lithium secondary
25 battery [$\text{V}_2\text{O}_5 \parallel \text{LiBF}_4/\text{PC}+\text{DME} \parallel \text{Li-Al}$], a lithium cobaltate-carbon secondary battery [$\text{LiCoO}_2 \parallel \text{LiPF}_6/\text{EC-DEC} \parallel \text{C}$], etc.

 Among these batteries, the lithium battery is a battery using lithium metal or a Li

alloy as an anode. Since lithium itself is light and can be used to generate a high voltage, a lithium battery offers the highest theoretical chance to obtain high voltage and energy density, and thus wide and extensive studies have been made all over the world since early 1960s. The basic performance of a lithium battery is decided by cathode-active materials, and thus various cathode-active materials have been proposed. For example, a fluorinated graphite-lithium battery using a fluorinated graphite as a cathode is considered as a good battery having a high energy density of five to ten times and voltage (about 3 volts) of about two times, compared to a manganese dry battery.

Lithium primary batteries generally employ either an anode made of lithium metal and cathode made of halides or oxides such as, for example, $(CF)_n$, MnO_2 , Ag_2CrO_4 , CuS , V_2O_5 , $SOCl_2$, SO_2 , CuO , FeS_x , $Bi_2Pb_2O_5$, P_2VP , PbI_2 , etc.

Commercially available lithium primary batteries employ a wound type anode in which a lithium foil is wound several times or a bobbin type anode in which a lithium foil is wound one time, and various cathode-activating materials. Although lithium primary batteries further broaden their applications to power source for fire-warning facilities, an alarm signal generator for an emergency case, or the like, thanks to their good and long storage and high voltage (3-4 volts). However, their poor high-temperature storage stability and voltage dropping problem on instantaneous discharging make it difficult for them to be used in other areas.

Rechargeable lithium batteries are classified into three types: a lithium metal battery which uses lithium metal as an anode, a lithium ion battery which uses carbon as an anode and liquid organic solvent as an electrolyte, and a lithium polymer battery which uses a solid electrolyte such as polymeric material.

Charging and discharging of lithium metal secondary batteries are achieved by a dissolution and deposition of lithium at the anode. In this regard, use of an anode made of lithium metal has an advantage that it is electrochemically efficient due to a uniform dissolution of lithium on discharging. However, it is also has a disadvantage that lithium metal grows and deposits in a dendrite shape (i.e., branch shape) on alternate repetition of

charging and discharging, thus resulting the problems of inner short circuit and reduced the charge and discharge efficiency of the battery.

The deposition of lithium metal in the form of a dendrite means that lithium metal does not grow or deposit uniformly on the surface of the anode. The growth of lithium in the form of a dendrite causes an inner shortage circuit through separators, and separation of lithium on discharging to shorten the cycle life of batteries. Therefore, secondary batteries subjected to repetition of charging and discharging sometimes do not employ lithium metal but use a lithium alloy as an anode material. In such case, a lithium alloy is electrochemically formed up on charging of the battery, thus avoiding the deposition of lithium on the surface of the anode.

It has been reported that about 1 % of lithium in the anode is lost on each cycle of charging and discharging. Therefore, it can be calculated that all the lithium in the anode will be lost after about 200 ~ 300 times of charging and discharging cycles even though the amount of lithium doubles its necessity. The use of lithium metal in an anode in much greater amount than that normally required has an economic problem as well as a reduction of the overall battery capacity because the lithium anode would take excessive volume in a limited space of a battery.

Recently, a lithium secondary battery such as a lithium cobaltate-carbon secondary battery has been proposed, which employs carbon having a stratified structure capable of carrying out reversible intercalation/deintercalation of lithium ion as an anode, instead of using lithium metal which is the most ideal in view of energy density and voltage or using a lithium alloy which is free from the problems involved with charging process. In such case, since lithium is present in the form of an ion, there are advantages that the battery stability is significantly increased, no formation of lithium dendrite on the surface of the anode is observed, and rapid charging of the battery is possible. However, it is difficult to avoid capacity reduction of the battery since the theoretical capacity density of carbon is 372 mAh/g, but its reversible capacity density is much less than the former, specifically is merely 1/10 of that of an anode made of lithium metal.

Meanwhile, lithium metal is an alkali metal belonging to IA Group in the Periodical Table of Elements. Due to its high reactivity, lithium cannot be stored in the atmospheric condition. Specifically, since lithium can explosively react with water contained in the atmosphere, any contact with water should be prevented during storage. In a drying room with a humidity of not more than 2 %, lithium reacts with a trace of water or oxygen in the atmosphere to form a thin layer of lithium compounds such as LiOH or Li₂O on its surface. An overgrowth of such layer may decrease the performance of high-rate discharge of the battery as well as the function of lithium metal as an anode.

As stated above, the use of lithium metal as an anode is the most preferable in terms of the electrochemical efficiency of a lithium battery. However, the use of lithium metal as an anode is significantly restricted due to the precipitation of lithium metal in the form of dendrite and a low efficiency upon charging and discharging. Further, a low reactivity in the form of lithium foil and the presence of a solid electrolyte interface (SEI) on the surface of the foil are believed to cause a voltage drop and a problem on high-rate discharging in a lithium primary battery.

The inventor has found that, when a lithium anode is prepared by using lithium powder which is obtained under oxygen-free and anhydrous atmosphere and sintered or cast on a metallic collector (a copper or aluminum foil or an exmet), the performance of a lithium primary battery is improved and the growth of lithium dendrite in a lithium secondary battery is suppressed.

DISCLOSURE OF INVENTION

The first object of the present invention is to provide an anode made of lithium powder for lithium battery comprising a flexible metallic base and a layer of lithium powder attached thereon, which is obtained under an anhydrous and oxygen-free atmosphere.

In one embodiment of the present invention, the anode made of lithium powder has a sleeve or strip shape and is attached on a flexible metallic base by sintering, rolling or molding.

The second object of the present invention is to provide a method for the preparation of an anode made of lithium powder for lithium battery, which comprises preparing lithium powder under oxygen-free and anhydrous atmosphere, and either shaping said powder into an appropriate shape or attaching said powder on a base (support).

5 In one embodiment of the present invention, the lithium powder obtained under oxygen-free and anhydrous atmosphere is attached on a metallic exmet or foil (aluminum or copper foil) to form an anode made of lithium powder, thus avoiding problems for shaping the anode into a desired shape while maintaining mechanical properties such as malleability, ductility or the like without losing powdery characteristics.

10 In another embodiment, lithium powder is mold-shaped into a sleeve shape or sintered into a strip shape to prepare an anode made of lithium powder.

The anode made of lithium powder of the present invention has good mechanical properties such as ductility, malleability and the like, and thus does not cause any mechanical problems even in case of a wound type anode or a bobbin type anode.

15 The third object of the present invention is to provide a primary and secondary lithium battery using an anode made of lithium powder described above.

(Overall process of preparing an anode of lithium powder)

20 In the context of the present invention, the term "layer of lithium powder" does not mean that lithium metal should be present in the form of powder. Said term rather means that lithium layer is prepared from lithium powder and still has a powdery feature. Specifically, since said layer of lithium powder can be prepared on a metallic base by sintering, rolling or mold-shaping lithium powder, particles of the lithium powder can be conglomerated in many cases. An example of said powdery feature can be envisaged by
25 the shape shown in the attached Figures 8 and 10, which are taken by an optical microscope.

In the present invention, lithium powder prepared under oxygen-free and anhydrous atmosphere is sintered to produce an anode for lithium battery. Thus prepared anode materials can replace conventional anode materials in the form of foil.

When the lithium powder of the present invention is used as an anode material for a lithium primary battery, its powdery feature having a high surface area facilitates the reaction of lithium metal with an electrolyte and thus decreases a voltage drop on a high-rate instantaneous discharge. Therefore, prepared batteries can be favorably used in various applications. Further, since the solid electrolyte interface (SEI) attained during its production process has a dense structure, they have an advantage of long term storage capacity.

When lithium powder of the present invention is used as an anode material for a secondary lithium battery, it is confirmed that the deposition and growth of a lithium dendrite is suppressed upon the repetition of the charging and discharging of battery. The reason for such improvement is assumed that the reaction area for lithium ions is increased due to its powdery feature and the solid electrolyte interface (SEI) of the powder is more dense and uniform. Such reasoning is supported by the fact that the smaller the mean particle size of the lithium powder is, the less the growth of lithium dendrite is.

According to the present invention, lithium powder which have almost never reacted with oxygen and/or water can be prepared by emulsifying molten lithium metal in an inorganic oil such as silicone oil, which does not substantially contain oxygen and/or water.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will further illustrated by reference of the accompanying drawings as follows:

Figure 1 is a sectional overview of a preparing equipment which can be used for the preparation of lithium powder under oxygen-free condition according to the present invention.

Figure 2 is a brief view of a pressing equipment which can be used for the preparation of lithium strip from lithium powder.

Figure 3 is a front sectional view of a battery constituting a lithium powder anode made of a lithium strip which is prepared to test the battery performance.

Figure 4a is a voltage vs. time plot showing the voltage dropping phenomena on instantaneous discharging of 10 days/15 times for MnO_2/Li type primary batteries comprising either a lithium foil anode of prior art or a lithium powder anode of the present invention, as an anode material. The conditions of the pulse discharge are that stand-by current is 0.003mA (0.0038mA/cm²) and run current is 9mA (11.5mA/cm²).

Figure 4b is a voltage vs. time plot showing the voltage dropping phenomena on instantaneous discharging of 60°C/17 days/100 times for the MnO_2/Li type primary batteries, which are the same as in Figure 4a.

Figure 5a is a voltage vs. time plot showing the voltage dropping phenomena on instantaneous discharging of 10 days/100 times for SOCl_2/Li type primary batteries comprising either a lithium foil anode of prior art or a lithium powder anode of the present invention, as an anode material. The pulse conditions are the same above the figure 4a.

Figure 5b is a voltage vs. time plot showing the voltage dropping phenomena on instantaneous discharging of 20 days/100 times for the same SOCl_2/Li type primary batteries as in Figure 5a.

Figure 6a is an internal resistance vs. time plot showing a change of the internal resistance of an anode electrode along the dipping time of the electrode in an electrolyte solution for a lithium secondary battery, which uses either an anode made of lithium foil according to prior art or an anode made of lithium powder according to the present invention.

Figure 6b is an internal resistance vs. time plot showing a change of the internal resistance voltage of an anode electrode along the dipping time of the electrode in an electrolyte solution for a lithium primary battery of SOCl_2/Li type, which uses either an anode made of lithium foil according to prior art or an anode made of lithium powder according to the present invention.

Figures 7a to 7c show examples of anode-forming materials which can be manufactured with lithium powder according to the present invention.

Figure 8 is an optical microscopic photo of the anode materials of an Example of the present invention after 5 cycles of charging and discharging.

Figure 9 is an optical microscopic photo of the anode materials of Comparative Example (foil specimen) of the present invention after 5 cycles of charging and discharging.

Figures 10, 11 and 12 are optical microscopic photos of the anode materials of the Examples 8, 9 and 10 of the present invention.

Figure 13 is charge efficiency vs. cycle plot showing the charge and discharge efficiency of a lithium secondary battery, which uses either an anode made of lithium powder or an anode made of lithium foil.

The numbers described in all the drawings are defined as follows: Li powder (1), Mixer part (2), Settler part (3), Press device (4), impeller (5), heater (6), mineral oil (7), circulating path of the mineral oil (8), opening for recovering Li powder (9), molten Li (10), suction opening (11), partition wall (11), overflowing opening (13), lower die (21), cylindrical mold (22), upper die (23), a pressurizing protrusion (23a), metal foil (31), Li powder (32, 34), exmet (33), anode (35, 41), cathode (42).

In below, the present invention is further illustrated.

(Preparation of lithium powder)

Methods for the preparation of lithium powder are known in this field. However, as far as the applicant comprehends, there is no disclosure to use such lithium powder as an anode material for a lithium battery.

In the present invention, it is preferable to use lithium powder that is prepared under oxygen-free/anhydrous conditions and it is advantageous to use lithium powder having a small particle size.

As one example of preparation of lithium powder, USP 5,776,369, which is allowed to B. Troy Dover et al. and assigned to FMC Corporation discloses a preparation method of lithium or sodium metal powder having a particle size of 10 to 100 microns, which comprises adding lithium or sodium metal in a hydrocarbon oil, heating the resulting mixture

to the temperature higher than the melting point of the metal under a strong stirring to form an emulsion of the molten metal particles in the hydrocarbon oil, cooling the resulting emulsion to obtain the molten metal particles in the form of solid particles, and filtering and washing the resulting solid particles to obtain lithium or sodium metal powder.

5 As an another example of preparation of lithium powder, the Korean Patent Application 1994-1781 filed by the present applicant can be mentioned, of which content is included here for reference.

Figure 1 describes an overview of an equipment for the preparation of lithium powder as disclosed in said Korean Patent Application No 1994-1781, which can be used for
10 the preparation of lithium powder usable in the present invention.

A process to prepare lithium powder using the equipment featured in Figure 1 consists of an emulsification step at the mixer part (2), a solidification step at the settler part (3), and subsequent separation and washing steps. At the mixer part (2), lithium metal is molten and mixed with mineral oil, and then stirred to form emulsified molten particles, and
15 in settler part (3), the molten lithium metal particles are solidified to form dispersed solid particles. After being separated and washed, lithium metal is obtained in the form of powder. To accomplish such, the temperature at the mixer part is set to temperature higher than that of the melting point of lithium metal, and the temperature at the settler part is set to temperature lower than that of the melting point of lithium metal so that lithium metal
20 particles formed at the mixer part can be solidified.

In the emulsification step, the molten lithium metal (10) and a mineral oil (7) flow via a suction opening (11) into the mixer part (2), and then form an emulsion by the rotating action of an impeller (5). Thus prepared emulsified particles of molten lithium metal including the mineral oil are transferred via an overflow opening (13) to a settler part (3), by
25 the rotating action of the impeller (5).

In the solidification step, since the temperature of the settler part is set to temperature lower than that of the melting point of lithium metal, the emulsified particles (1) of molten lithium metal are solidified according to the lapse of time to become dispersed

solid particles, which then move to the upper region of the mineral oil (7).

In the separation step, the dispersed solid particles moved to the upper region are collected via an opening for recovering Li powder (9) and the mineral oil is washed off. The mineral oil remained in the settler part is circulated into the mixer part. For achieving
5 such separation, the volume ratio of molten Li : mineral oil at the mixer part is not specifically limited, but it is preferable to have a ratio of about 1 : 10~20.

In the equipment as described above, the surface of the molten lithium droplets, which are freshly developed by the bursting of the liquid phase of bulk molten lithium metal, is directly covered with mineral oil (7) having no dissolved oxygen. Thus the particles of
10 molten lithium metal are cooled to room temperature and get solidified under the oxygen-free condition by being covered with said mineral oil. Therefore, lithium powder (1) of the present invention is in fact prepared under oxygen-free conditions.

Lithium powder (1) prepared by the above described equipment have a contact with oxygen after the mineral oil (7) is washed at room temperature, and therefore, metal oxide
15 membrane can be formed only on the surface of the particles of lithium powder (1). Further, if the preparation and separation of lithium powder are carried out in a closed system such as a glove box in which a contact with outside atmosphere is blocked, a contact with oxygen can be restricted or prevented throughout the overall process for the preparation of lithium powder.

20 An exemplary embodiment of the process to prepare lithium powder is given below:

First, a heater is set such that the temperature at the mixer part (2) can be maintained at around 200°C which is 20°C higher than the melting point of lithium metal (about 180°C), and the temperature at the settler part (3) can be maintained at room temperature so that the molten particles (1) of lithium metal prepared at the mixer part (2) can be solidified.

25 When the setting temperature is achieved, the molten lithium metal (10) and a mineral oil (7) are introduced in a certain amount (for example, in a ratio of about 1 : 10 of Li : mineral oil) to the mixer part (2). The molten lithium metal (10) and mineral oil are

mixed in the mixer part (2) and emulsified by rotating action of an impeller (5) equipped on a motor (M) in high speed for 1 minute.

Thereafter, the emulsified lithium metal particles (1) and the mineral oil (7) are lifted to the upper region of the mixer part (2) by the rotation power of the impeller (5), and then the resulting overflow is transferred to the settler part (3). In the settler part (3), the emulsified particles of molten lithium (1) are solidified to dispersed particles of solid lithium metal. After a sufficient time lapse, the solidified lithium powder eventually separate from the mineral oil and then float in the upper region of the oil due to their low density.

The lithium metal particles (1) floating in the upper region of the oil are collected and washed with hexane to remove the mineral oil (7), and the remaining mineral oil in the settler part (3) is subjected to circulation into the mixer part (2).

The particle size of lithium powder which can be used in the present invention is not particularly limited, but is generally not more than 200 μm , preferably not more than 100 μm , and more preferably not more than 50 μm . As the particle size of lithium powder becomes larger, battery's current density during charge and discharge becomes lower and the dendrite formation becomes more favorable. Therefore, lithium particles having small size is preferred. The particle size of lithium powder prepared by the above-mentioned equipment is usually decided by the height and size of the overflow exit (13), the rotation velocity of the impeller (5), the number of blades of the impeller (5), the process time of emulsification step, etc. For example, when the impeller is driven at 30,000 rpm, lithium powder having about 20~30 μm of the particle size can be obtained.

The above process to prepare the lithium powder is given as an example, which by no means restrict the scope of the present invention.

(Anode for Lithium Battery and Preparation Method Thereof)

In general, an anode for a lithium battery is composed of a conductive metal base and a lithium metal layer attached thereon, which is made of lithium metal for lithium

primary batteries, but usually from lithium alloy in a foil shape for lithium secondary batteries.

In the present invention, said lithium metal layer is constructed as lithium powder layer made of lithium powder.

5 The lithium powder anode according to the present invention is generally composed of a flexible metal base and a lithium powder layer formed on the surface of said metal base. Said flexible metal base may be either a conductive metal strip or a metal exmet. Said lithium powder layer on said flexible metal base may be formed in either a strip shape or a sleeve shape, and attached onto said conductive metal base by sintering, compressing or
10 molding process.

 Since lithium is a soft metal having a high ductility, it does not require an excessive heating or pressure for sintering, compressing, rolling or molding process. In general, the sintering and rolling can be carried out at room temperature, and it is preferable to carry out the rolling or compressing after annealing with a slight heating is firstly done.

15 In one embodiment, the recovered lithium powder is washed with pentane or hexane to remove the mineral oil covering the powder, and then attached onto various conductive metal strips such as, for example, Al or Cu strips and sintered to prepare an anode material having a strip shape. Thus prepared strip is wound several times to obtain an anode of wound type, or a single time to obtain an anode of bobbin type.

20 Alternatively, the above washed lithium powder is attached onto a metal exmet to prepare an anode material, which may be wound to obtain an anode of wound type or bobbin type. In addition, it is possible to prepare a cylindrical anode by directly molding the above lithium powder.

 Exmets are generally used as a support for a lithium foil for manufacturing batteries.
25 The use of exmets facilitates the winding process. When it comes to the preparation of the anode made of lithium powder according to the present invention, exmets are very useful.

 In general, metal powder by itself can be sintered or rolled to prepare a strip, but the ductility and malleability of the metal may be deteriorate according to the process conditions,

especially considering that a sintering under excessive pressure may cause the loss of powdery features of the metal. Therefore, if an anode material is formed in a strip by sintering or rolling lithium powder while merely maintaining the required mechanical properties of the strip, the resulting strip of the anode material may get broken or cracked during the winding process to obtain the anode of a wound type or bobbin type.

An anode material made of lithium powder according to the present invention does not cause such problems when it is shaped into an anode of wound type or bobbin type, since its powdery properties are well maintained and its mechanical properties such as ductility and malleability are strongly preserved after the shaping into an anode.

(Preparation of lithium metal strip)

Preparation of lithium metal strip as an anode material can be carried out using an equipment as shown in Figure 2, for example.

As shown in Figure 2, a lower die (21) is combined with a cylindrical mold (22), a upper die (23) having a pressurizing protrusion (23a) inserted into the cylindrical mold (22) is pressed downward. The pressing may be carried out by suing a oil-pressure press or a roller.

An appropriate amount of lithium powder (about 0.1 g) is charged in the cylindrical mold (22), and pressure of about 10kgf/m² is applied to prepare a disc type lithium strip. The final thickness of the lithium strip can vary according to the type of batteries to be prepared. Thus the amount of lithium powder charged in the mold should be adjusted accordingly.

A lithium anode has a thickness of about 0.8 mm for a common battery and about 0.2 mm for a coin type battery. The amount of lithium powder to be used in the preparation of lithium powder strip is adjusted depending on said thickness.

The pressure of an oil pressure press can have an influence on the density of lithium powder strip and ultimately on the battery characteristics. In general, although low pressure can preserve the powdery features of lithium powder, it is not favorable in terms of

the mechanical properties of an anode. It is important to balance said two aspects in a suitable manner.

Fig 7a is a simplified drawing of a lithium powder strip prepared by attaching lithium powder (32) onto a conductive metal strip (31) such as Al or Cu, followed by sintering. This strip can be wound several times or a single time to prepare an anode of wound type or bobbin type, respectively.

Figures 7b is a drawing which shows an attachment of lithium powder on an exmet and a formation of an anode of wound type or bobbin type.

Figure 7c is a drawing which shows a formation of an anode in the form of sleeve by molding.

(Lithium battery)

A lithium battery is prepared by using an anode as prepared above in accordance with the known process.

A lithium primary battery using a strip-type anode made of lithium powder obtained according to the present invention carries surprising effects that an instantaneous high-rate discharge is possible and a voltage drop on discharging is significantly decreased, compared to conventional lithium primary batteries using a lithium anode of foil type.

Said effects are made possible by improvement in overall reactivity of the battery, i.e., an anode material in powdery form bears more surface area and the growth of SEI is better controlled than those in foil form, since the surface SEI of powder is more compact and stable than that of a foil. Due to such reasons, lithium batteries using an anode material made of lithium powder has a good long-time storage capability, good electrochemical characteristics such as a high-rate discharge, a voltage drop on discharging, etc., and a high improvement in battery efficiency due to the increased surface area.

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention is further illustrated by the following Examples, which should

not be considered as a limitation of the scope of the present invention.

Example 1

In order to test a battery performance, a battery cell of MnO_2/Li type having a structure as shown in Figure 3 is prepared by using a Li anode made of a Li strip.

The working electrode (namely, anode) (41) of the above battery cell is made of Li powder prepared in a laboratory according to the present invention and the counter electrode (42) (namely, cathode) is made of MnO_2 commonly used in commercial cells. An electrolyte commonly used for an cell is introduced between both electrodes in a certain amount (about 1 mL)

The designated numbers shown in Figure 3 represent a cylindrical casing (43) made of teflone, a ring (44) made of teflone, and an upper casing and a lower casing (45 and 46) made of SUS 316.

After constructing such battery cells, each cell is subjected to the following discharging test by using a WBCS3000 charging and discharging machine (Won-A tech Co., Korea).

Figure 4a shows the result of a voltage dropping test of the MnO_2/Li battery cell of the present invention, when fifteen instantaneous dischargings are carried out after 10 days lapse from the preparation.

Comparative Example 1

A comparative battery cell having the same structure with Example 1 is prepared except that an anode made of a Li foil prepared according to a conventional method is used. Figure 4a shows the result of a voltage dropping test of the comparative battery cell subjected to the same charging and discharging test with Example 1.

As it can be seen from Figure 4a, an average voltage dropping of 0.627 V is measured for the battery cell of Example 1, whereas an average voltage dropping of 0.802 V is measured for the battery cell of Comparative Example 1.

Example 2

In order to carry out an equatorial passing test (namely, high temperature storage test), a battery cell of MnO_2/Li type prepared by the same method with Example 1 is subjected to a test wherein the battery cell is stored at 60°C for 17 days and then subjected to 100 instantaneous discharges, in order to determine the voltage dropping of the cell. The result is shown in Figure 4b.

Comparative Example 2

The same battery cell with Comparative Example 1 is subjected to the same test with Example 2 to determine the voltage dropping on instantaneous discharging of the cell. The result is shown in Figure 4b.

Example 3

A battery cell of SOCl_2/Li type prepared by the same method with Example 1 except that carbon is used as a cathode is subjected to a test wherein the battery cell is stored for 10 days and then subjected to 100 instantaneous discharges to determine the voltage dropping of the cell. The result is shown as a graph in Figure 5a.

Comparative Example 3

A battery cell of SOCl_2/Li type prepared by the same method with Example 1, except that the anode made of a Li foil in Comparative Example 1 and a Li/SOCl_2 cathode are used, is subjected to the same test with Example 3 to determine the voltage dropping on instantaneous discharging of the cell. The result is shown in Figure 5a.

Example 4

The same test with Example 3 except that a battery cell is stored for 20 days is

carried out and the result is shown in Figure 5b.

Comparative Example 4

The same test with Comparative Example 3 except that a battery cell is stored for 20 days is carried out and the result is shown in Figure 5b.

As it can be seen from Figures 4a to 5b, for both cells stored for 1 to 20 days and cells stored at high temperature, the battery cells of the present invention have much better performance than those of comparative examples using an anode of foil type. In addition, the cell voltage of Comparative Example 2 drops below 0 V in a high-temperature test, which means a damage of the battery and a severe voltage delay.

Example 5

A secondary battery is constructed by using a solvent mixture of EC (ethylene carbonate)-DMC (dimethyl carbonate) (1:1) containing LiPF_6 (1M) and an anode made of Li powder. A change of the internal resistance (that is, a resistance of the surface film of the anode) of the above secondary battery with the lapse of immersion time, during which the anode is immersed in the electrolyte, is determined by using a IM6 (Zahner company, Germany). The result is shown in Figure 6a.

The internal resistance in Figure 6a is determined by measuring a diameter of a semi-circle in a cole-cole plot, which represents a resistance of the surface film of an electrode.

Comparative Example 5

The same battery cell with Example 5 except that an anode made of a Li foil is used is subjected to the same test with Example 5 to determine a change of the internal resistance. The result is shown in Figure 6a.

Example 6

The same battery cell with Example 3 is subjected to the same test with Example 5 to determine a change of the internal resistance with the lapse of immersion time during which the anode is immersed in the electrolyte (SOCl_2). The result is shown in Figure 6b.

Comparative Example 6

The same battery cell with Comparative Example 3 is subjected to the same test with Example 5 to determine a change of the internal resistance with the lapse of time during which the anode is immersed in the electrolyte (SOCl_2). The result is shown in Figure 6b.

As can be seen in Figures 6a and 6b, the anodes made of a Li foil has a low initial resistance, but shows a very high resistance with the time lapse since a solid electrolyte interface grows as the time lapses. On the other hand, the anode made of Li powder has an initial resistance higher than that of the Li foil, but shows a very slow increase in the resistance and eventually has little increase after several days compared to the initial value. As a result, it has much lower resistance than that of a Li foil. This means that a solid electrolyte interface of lithium powder is more dense and uniform than that of a Li foil and it does not grow further. Therefore it can be predicted that a voltage dropping on discharging is not significant even after a long-term storage. In addition, it can be expected that the growth of dendrite is prohibited since lithium metal can deposit in a uniform manner when the battery is charged.

Example 7

Lithium powder having an average particle size of 50 μm is sintered and used as an anode material to construct a semi-cell. Thus obtained cell is subjected to a battery test under a charging/discharging condition of 1.25 mA/cm^2 / 1.25 mA/cm^2 with 5 cycles. After the test, the surface structure of the anode is observed with an optical microscope to check

the growth of lithium dendrite. The result is shown in Figure 8.

Comparative Example 7

A lithium ingot is extruded into a foil, which is used as an anode material to construct a semi-cell. Thus obtained cell is subjected the same battery test and observation as in Example 7. The result is shown in Figure 9.

Example 8

The same battery test and observation as in Example 7 is carried out except that the charge/discharge conditions are 1.25 mA/cm² / 6.0 mA/cm². The result is shown in Figure 10.

Example 9

The same battery test and observation as in Example 7 is carried out except that the average particle size of lithium powder is 70 μm. The result is shown in Figure 11.

Example 10

The same battery test and observation as in Example 8 is carried out except that the average particle size of lithium powder is 70 μm. The result is shown in Figure 12.

Example 11

A secondary battery is constructed by using a commonly used cathode material (sintered LiCoO₂), an electrolyte (EC:DMC=1:1, LiPF₆ 1M), and an anode made of Li powder or an anode made of a lithium foil. Each battery cell is subjected to 20 cycles of charging and discharging to determine the cycle efficiency of the battery (discharging rate/charging rate 1.3 mA (1/5C)). The results are shown in Figure 13.

As can be seen from the above results, the growth of lithium dendrite was observed

for an anode made of conventional strip-type metal (see the dark area in Figure 9), whereas the growth of lithium dendrite is suppressed in an anode made of sintered lithium powder of the present invention (see Figure 8). In addition, no growth of lithium dendrite is observed in an anode made of lithium powder having an average particle size of about 50 μm even under harsh conditions, for example under the charging condition of 6.0 mA/cm² as in Example 8 (see Figure 10).

However, from the results of Examples 9 and 10, it can be concluded that, as the particle size of lithium powder increases, the possibility for the growth of lithium dendrite becomes larger; for example, the growth of lithium dendrite is observed in an anode made of lithium powder having an average particle size of about 70 μm under the charging condition of 6.0 mA/cm² (see Figure 12).

As can be seen from Example 11 wherein the test of up to 20 cycles of charging and discharging is carried out, a battery cell with an anode material made of lithium powder has a high efficiency with no loss of the battery capacity, whereas a battery cell with an anode material made of lithium foil shows 10 to 20 % loss of the battery capacity per cycle, after running 10 cycles.

Based on the observation that the growth of lithium dendrite is suppressed better as the average particle size of the lithium powder decreases, it may be concluded that the suppression of the growth of lithium dendrite in the anode of the present invention originates from the fact that the reaction area and the properties of the solid electrolytic interface on the lithium surface are different in the present invention in which the powdery anode material is utilized.

It is understood that the foregoing detailed description including the specific and preferable embodiments is given as a way of illustration of the invention and many variations and modifications can be made therefrom by those skilled in the art without departing from the spirit of the present invention.

INDUSRIAL APPLICABILITY

When an anode made of lithium powder according to the present invention can be used, the high-temperature storage stability and the voltage dropping on instantaneous discharging can be improved for a lithium primary battery. And for a secondary lithium battery, the deposition and growth of lithium dendrite on charging and discharging can be suppressed, and thereby the efficiency of charging and discharging can be greatly improved to avoid the battery capacity reduction and the possibility of shortage of battery.

The anode material of the present invention can be prepared without losing its powdery features of the lithium powder layer while still maintaining its mechanical properties such as ductility and malleability. Therefore, deterioration problem of mechanical properties of an anode, which occurs for an anode of wound type or bobbin type, does not exist in the anode of the present invention.

What is claimed is:

1. An anode for a lithium battery comprising a flexible metallic base and a layer of lithium powder attached thereon.

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2. The anode according to claim 1, wherein the lithium powder has a mean particle size of not more than 100 μm .

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3. The anode according to claim 1 or 2, wherein the metallic base has a shape of either a conductive strip or an exmet.

4. The anode according to claim 1 or 2, wherein the strip or exmet is wounded a single time or several times to form an anode of wound type or bobbin type, respectively.

15

5. The anode according to claim 1 or 2, wherein said lithium powder is prepared by melting lithium metal under oxygen-free/anhydrous conditions, stirring said molten lithium metal in mineral oil which has been heated to the temperature higher than the melting temperature of lithium metal to form an emulsion of the molten lithium metal, cooling the emulsion to solidify the emulsified particles of the molten lithium metal, and optionally separating and washing the resulting lithium powder.

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6. The anode according to claim 1 or 2, wherein the lithium battery is a lithium secondary battery.

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7. A method of preparation of an anode for lithium battery, comprising attaching lithium powder on a metal exmet and winding the resulting metallic exmet.

8. A method for the preparation of an anode for a lithium battery, comprising molding and sintering lithium powder in a strip form, and winding the resulting strip around a flexible metallic base.

5 9. The method according to claim 8, wherein the lithium powder is attached onto the flexible metallic base by rolling.

10 10. A method for the preparation of an anode for a lithium battery, comprising molding lithium powder in a sleeve form.

11. A primary or secondary lithium battery comprising a cathode, an anode and an electrolyte, characterized by that the anode for a lithium battery according to claim 1 or the anode for lithium battery prepared according to any one of claims 7 to 10 is used as an anode.

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FIG. 1

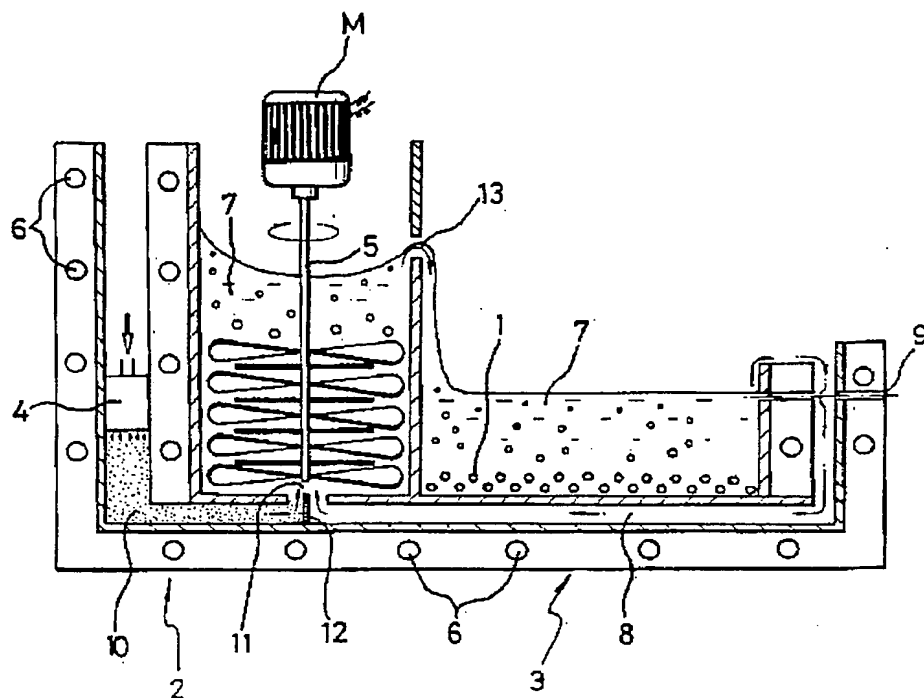


FIG. 2

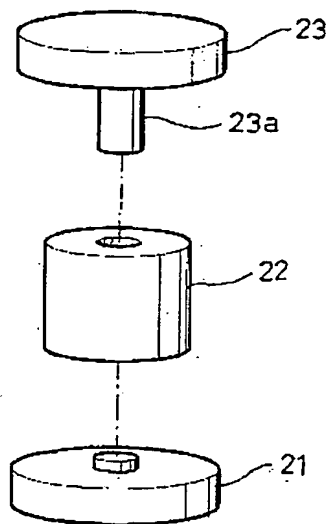
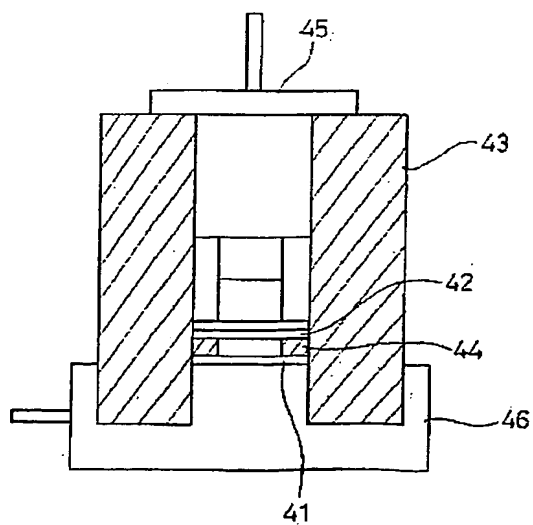
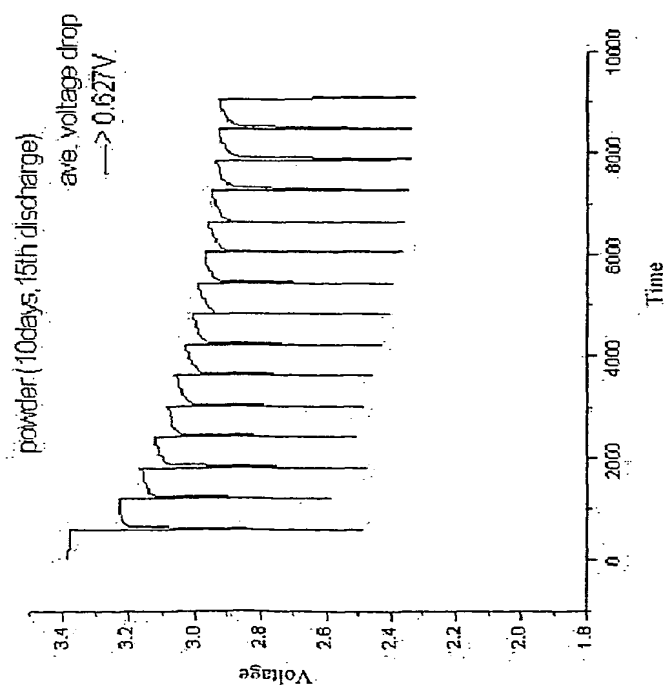
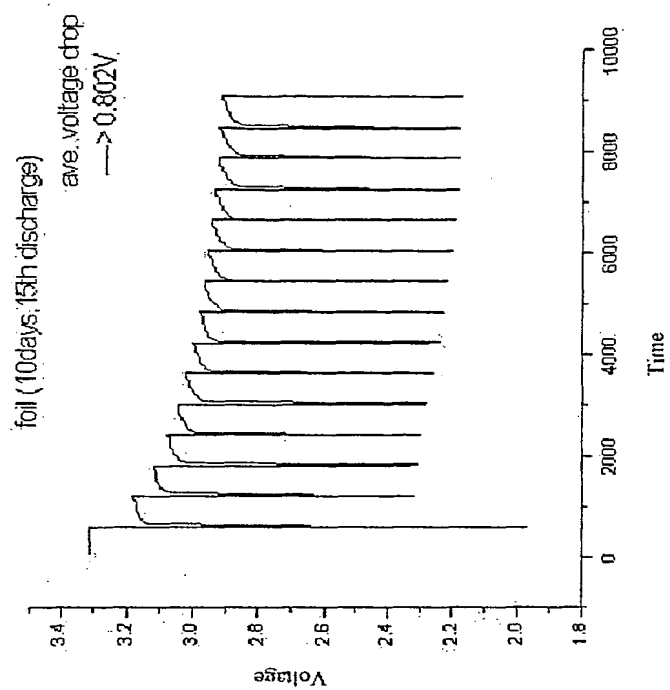


FIG. 3



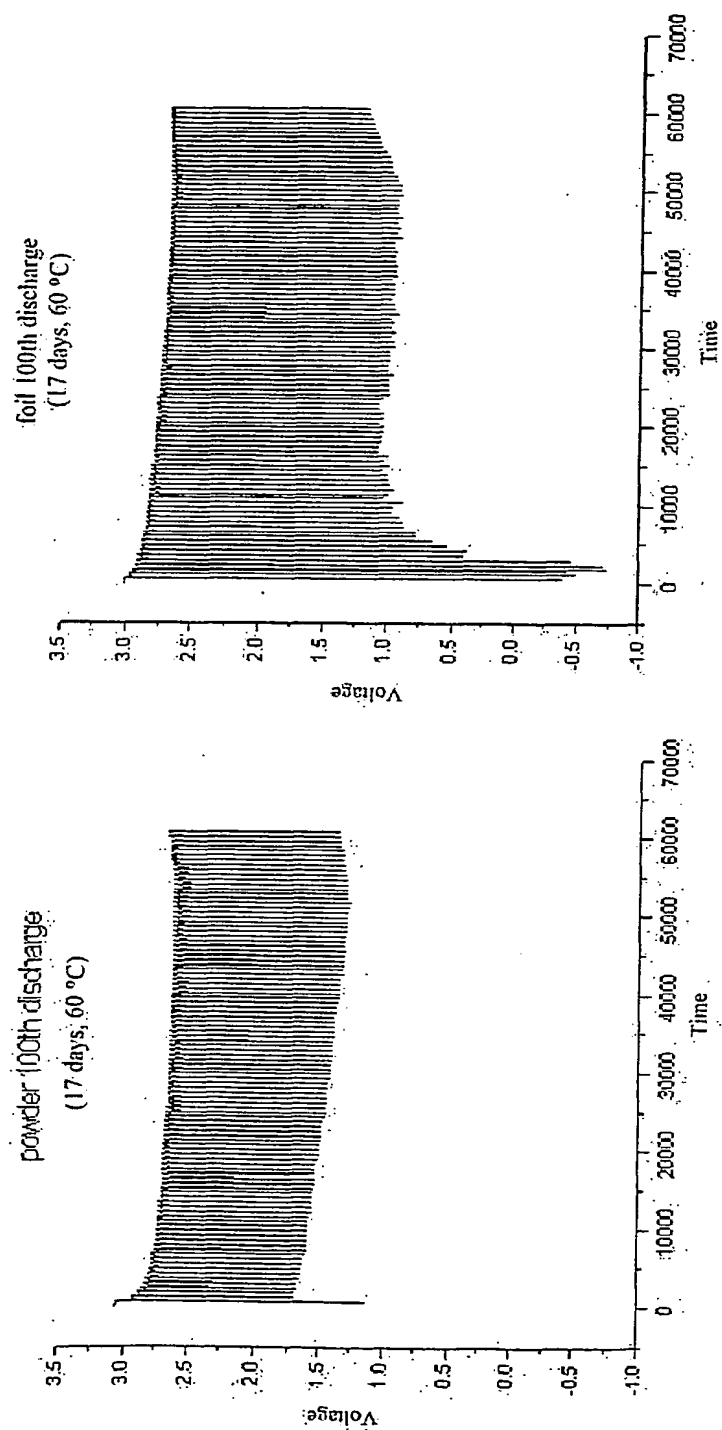
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FIG 4A



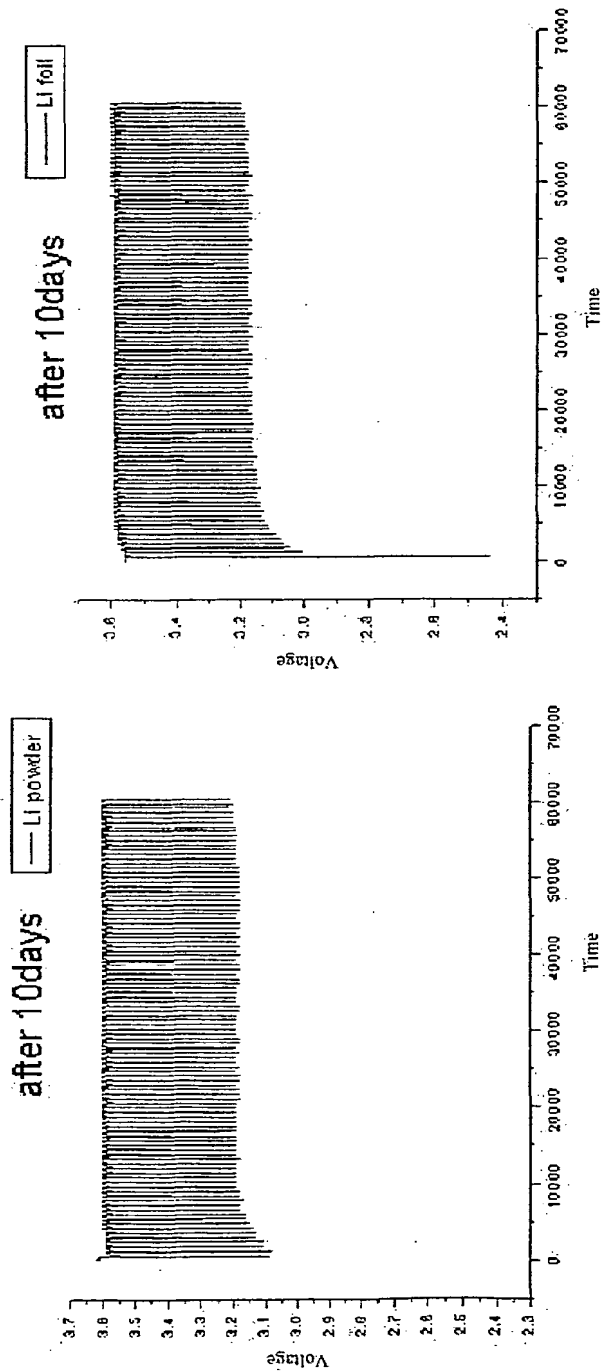
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Fig. 4B



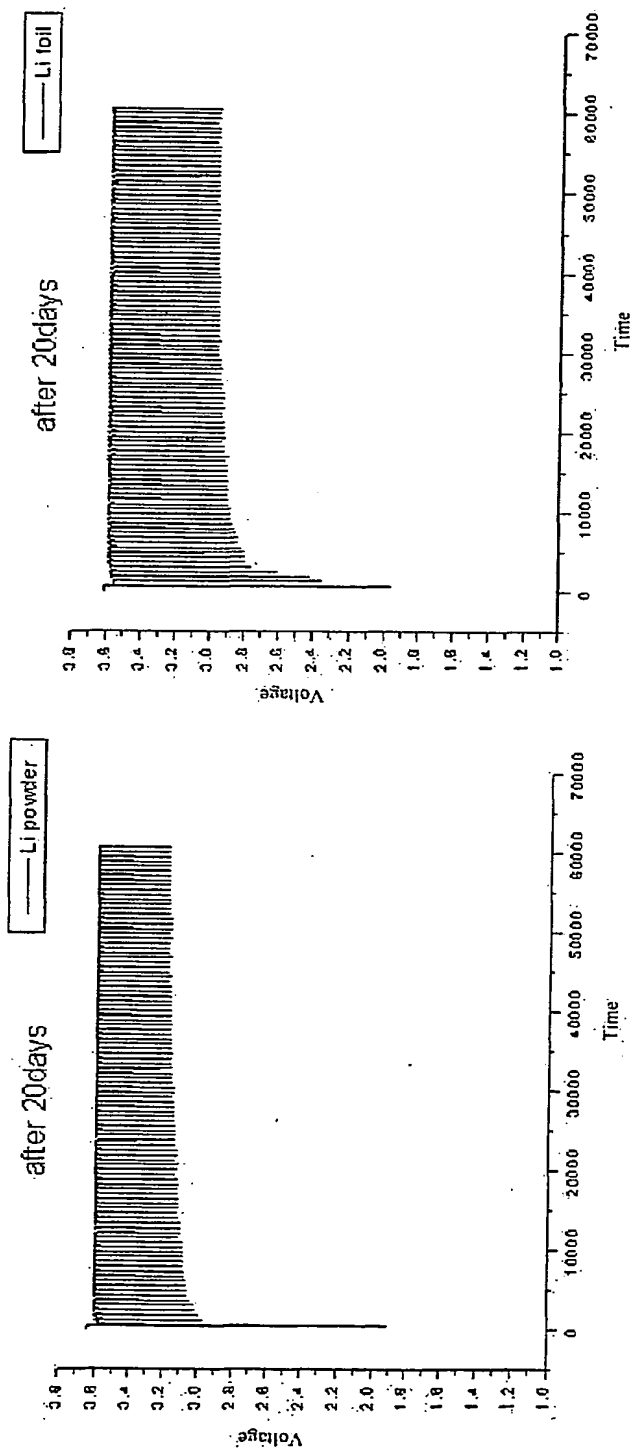
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Fig. 5A



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Fig. 5B



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Fig. 6A

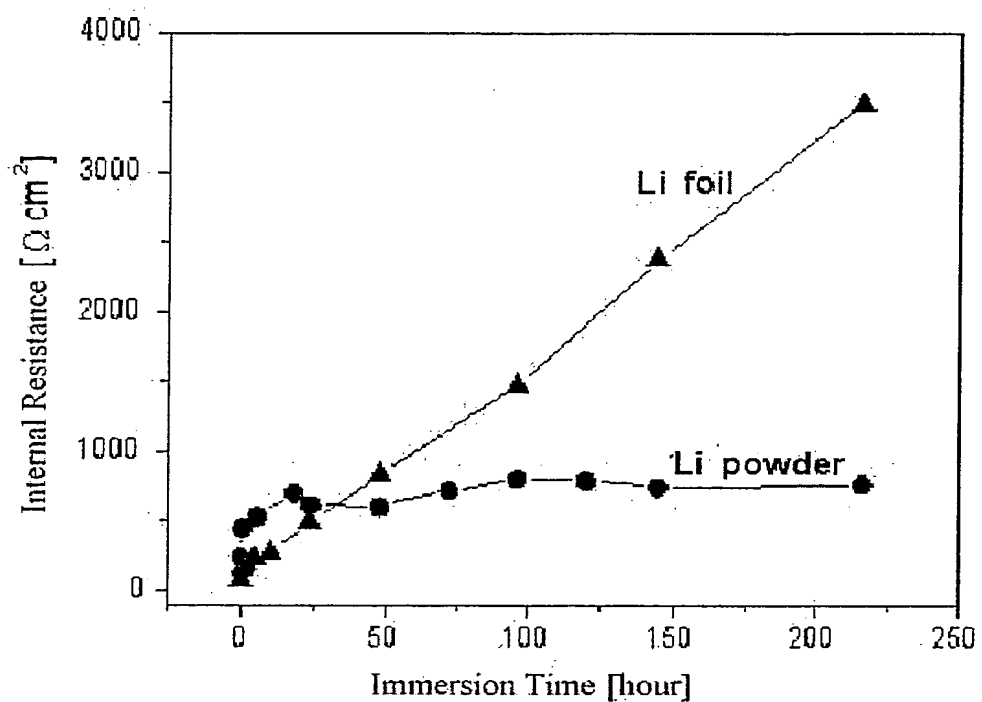
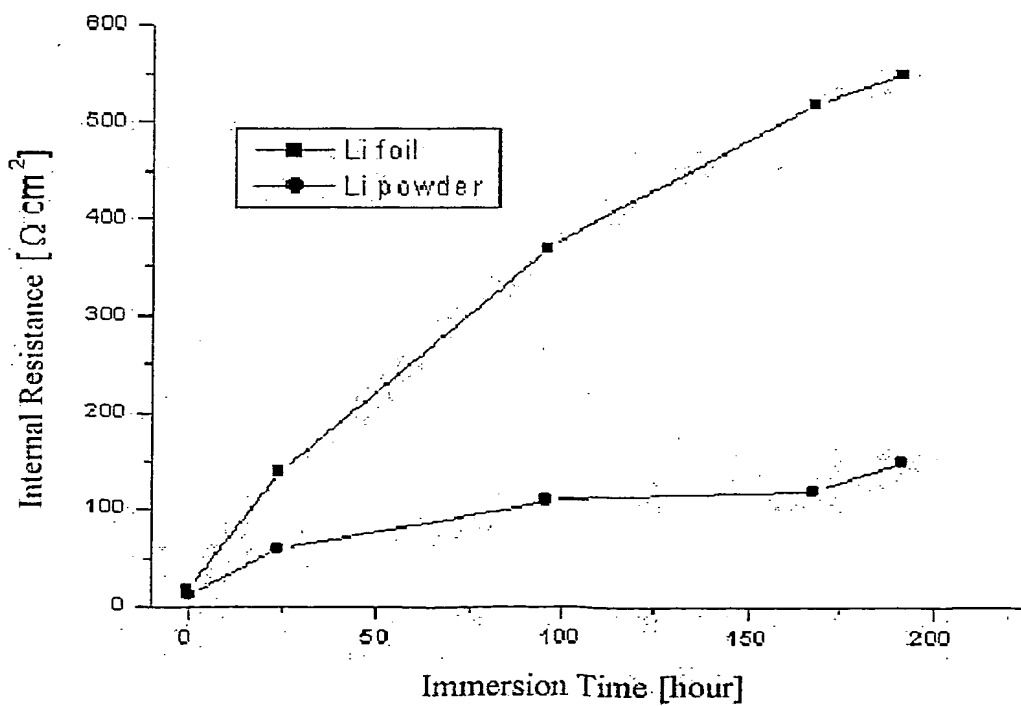


Fig. 6B



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FIG 7A

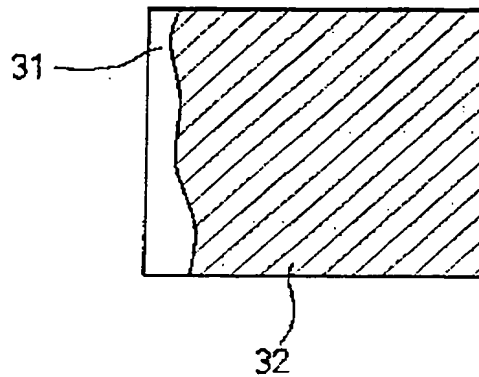


FIG 7B

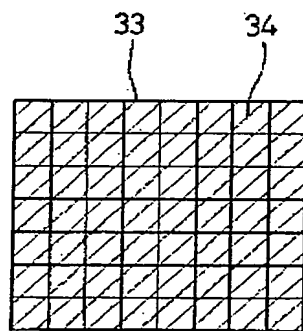


FIG 7C

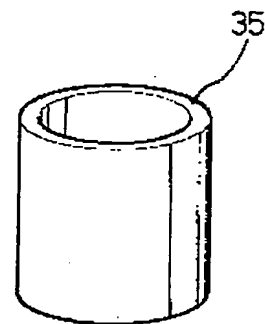


FIG 8

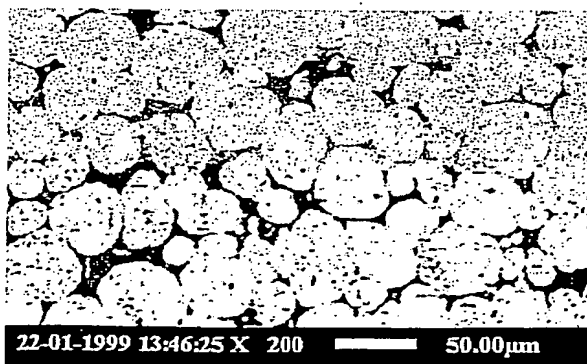
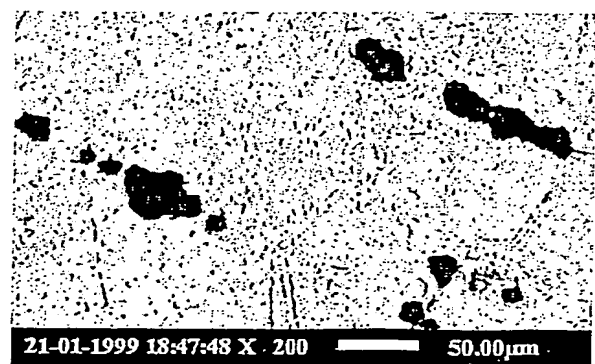


FIG 9



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FIG 10

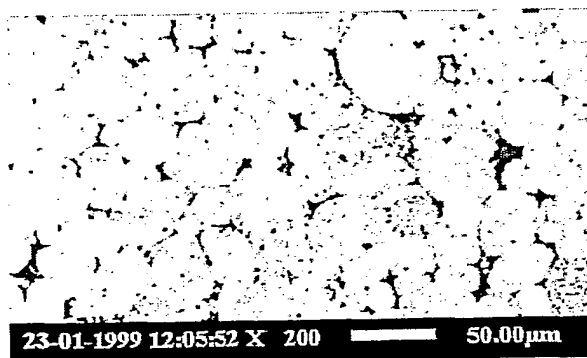


FIG 11

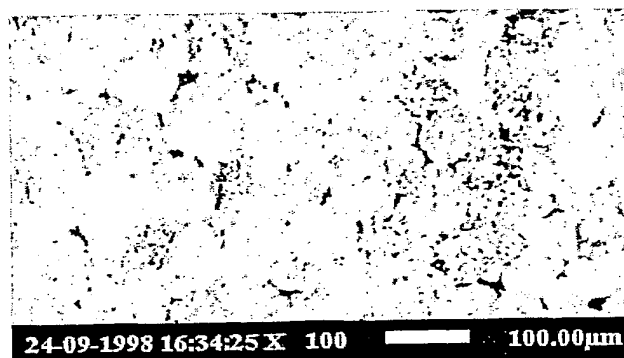


FIG 12

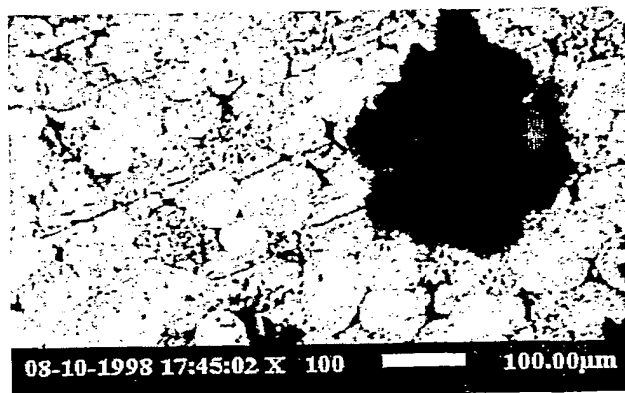
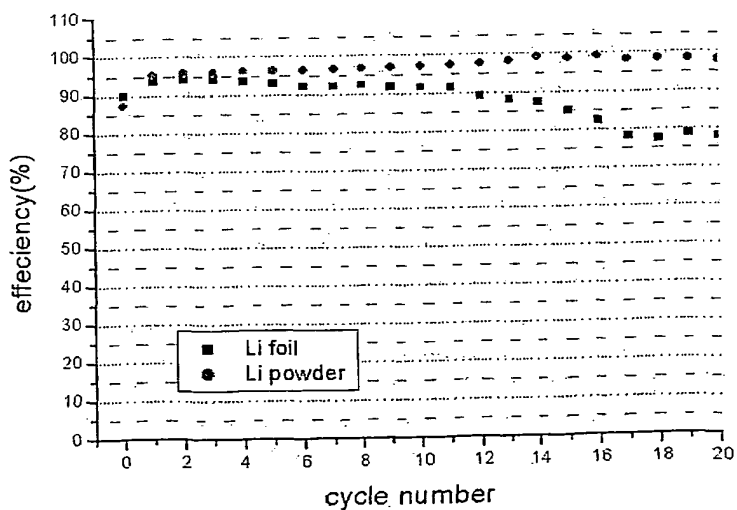


FIG 13



INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR00/01001

A. CLASSIFICATION OF SUBJECT MATTER**IPC7 H01M 12/00**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7 : H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

USPAT, FPD, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 5776369 (FMC CORPORATION) JULY 7, 1998 SEE THE WHOLE DOCUMENT	1-11
A	JP, A, 59143268 (HITACHI MAXELL LTD.) AUGUST 16, 1984 SEE THE WHOLE DOCUMENT	1-6
A	JP, A, 57065670 (SANYO ELECTRIC CO., LTD.) APRIL 21, 1982 SEE THE WHOLE DOCUMENT	1-6
A	JP, A, 59127376 (HITACHI MAXELL LTD.) JULY 23, 1984 SEE THE WHOLE DOCUMENT	1-6
A	JP, A, 61004162 (FUJI ELECTROCHEM CO., LTD.) JUNE 18, 1986 SEE THE WHOLE DOCUMENT	1-6

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search

22 MAY 2001 (22.05.2001)

Date of mailing of the international search report

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Name and mailing address of the ISA/KR

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